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AN EVALUATION OF CARBON STEEL CORROSION UNDER STAGNANT SEAWATER CONDITIONS

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ABSTRACT

Corrosion of 1020 carbon steel coupons in natural seawater over a six-month period was more aggressive under stagnant anaerobic conditions than stagnant aerobic conditions as measured by weight loss and instantaneous corrosion rate (polarization resistance). Under oxygenated conditions, a two-tiered oxide layer formed. The outer oxide layer was reddish-brown and contained numerous filamentous bacteria. The inner oxide was extremely tenacious and resistant to acid-cleaning. Under anaerobic conditions, a non-tenacious sulfur-rich corrosion product with enmeshed bacteria formed on carbon steel surfaces. In both aerobic and anaerobic exposures, corrosion was more aggressive on horizontally oriented coupons compared to vertically oriented samples. Bulk water chemistry and microbial populations were measured as a function of time. Despite the stagnant conditions, both were dynamic.

Keywords: Carbon steel, microbiologically influenced corrosion, sulfate-reducing bacteria, seawater, anaerobic

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INTRODUCTION

Hamilton¹ recently proposed a model for SRB corrosion of carbon steel in which sulfate, an intermediate electron acceptor, is reduced to sulfide. In his model, sulfide reacts with iron to form a corrosion product that ultimately transfers electrons to oxygen. According to Hamilton¹, oxygen is the electron acceptor for seemingly different microbiologically influenced corrosion mechanisms of ferrous metals. Consistent with that model, most reported cases of SRB induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium.^{2,3} Several investigators⁴⁻⁷ have demonstrated that natural marine biofilms form on metal surfaces, providing an anaerobic metal/biofilm interface and an environment for the growth of SRB, independent of bulk oxygen concentrations. Seawater contains 2 gm l⁻¹ sulfate than can be reduced to sulfide by SRB in the absence of oxygen. Others^{8,9} have demonstrated that the most corrosive operating condition is one in which carbon steel is exposed to alternating oxygenated/anaerobic conditions.

According to Hamilton's model, corrosion of carbon steel should be minimal in an anaerobic environment. Laboratory experiments were designed to test that hypothesis. Uncoated carbon steel was maintained under the following stagnant conditions: 1) natural seawater open to air and 2) anaerobic natural seawater. Results presented in this paper are limited to a six-month exposure.

METHODS AND MATERIALS

Identical chambers were built to expose 1020 carbon steel and natural seawater to the defined operating conditions (Figure 1). Cylindrical chambers (35.5 cm diameter and 27.9 cm height) were constructed from heavy gauge, chemical resistant, opaque polyethylene. Corrosion coupons were 1020 carbon steel (Table 1), 3.2 cm dia. x 0.16 cm thick (Metals Samples[®], Munford, AL) with an as-mill finish. Individual insulated wires were attached to the back of each sample and held in place using conductive silver adhesive (Electron Microscopy Sciences[®], Fort Washington, PA) and carbon tape.

The exposure side of the coupon was coated with vacuum grease and centered face down inside a plastic mount (1.25" dia. x 1" height). Samples were mounted in Epothin[®] epoxy (Buehler, Lake Bluff, IL) with the wire connection exposed to the epoxy. Vacuum grease prevented intrusion of epoxy between the sample face and the bottom of the mount and allowed the as-mill finish to be preserved. Prior to seawater exposure, coupons were rinsed in acetone, ethanol and distilled water and dried with nitrogen gas to removed vacuum grease and residual surface debris. Epoxy-mounted carbon steel coupons were orientated in rows both vertically (27 samples) and horizontally (9 samples), with the metal side up, in each chamber to simulate tank sidewalls and bottoms, respectively, for a total of 36 samples (Figure 2). As shown in Figure 1, a Ag/AgCl electrode and a platinum/niobium mesh were used as reference and counter electrodes, respectively. In all cases chambers were filled with natural seawater collected at the Naval Research Laboratory (NRL) Corrosion Facility, Key West, FL.

Chambers containing stagnant seawater were sealed and transported to NRL, Stennis Space Center, MS. The chamber filled with natural, oxygenated seawater was open to air via a one-inch tube in the chamber cover. The chamber filled with anaerobic water was maintained in an anaerobic hood with an atmosphere of 5% CO₂, 10% H₂ and the balance N₂. Natural Key West, FL seawater was deoxygenated using a premixed inert gas. The pH is lowered slightly because of CO₂.

Water samples from the stagnant chambers were collected every month to assess changes in dissolved and particulate water chemistry (dissolved oxygen, nitrogen in the form of ammonia, nitrate and nitrite, bulk pH, sulfide concentration, sulfate concentration, turbidity) using standard techniques (Acculab[®], Inc., Marrero, LA). Serial dilutions of liquid culture media (Dixie Testing and Products, Inc.[®], Houston, TX) were used to determine most probable numbers of acid-producing bacteria (APB), sulfate-reducing bacteria (SRB), general heterotrophic aerobes, and anaerobes.

Four coupons (1 horizontally and 3 vertically orientated) were removed monthly. Coupons were fixed in cacodylate buffered 4% glutaraldehyde in seawater, rinsed in distilled water and examined to assess the extent of biofilm formation and corrosion morphology. Environmental scanning electron

microscopy (ESEM) and energy dispersive spectroscopy (EDS) were used to characterize the corrosion morphology, biofilm structure and corrosion product composition on the metal surface.¹⁰ After ESEM evaluation, coupons were acid-cleaned¹¹, weighed for weight loss and re-examined. Open-circuit corrosion potential (E_{corr}) was monitored continuously using an Agilent® HP34970A data logger and linear polarization resistance was performed on each sample every 1-3 months. Dissolved oxygen (DO) in each container was monitored continuously using a dissolved oxygen electrode (OxyGuard® DO Probe, Port Moody, British Columbia, Canada) and a MadgeTech® mini data logger.

RESULTS

The DO concentration for the aerobic seawater fluctuated between 4 ppm and 1 ppm over the exposure period. The treated seawater had an initial DO concentration of less than 1 ppm and quickly dropped to 0 in the first couple of days. Changes in bulk water chemistry as a function of time for both exposure conditions are presented in Tables 2 and 3. In general, the concentration of sulfide in the bulk medium increased with time in both chambers. The final bulk sulfide concentration in the anaerobic seawater was consistently higher than that of the aerobic seawater. The sulfate concentrations declined in both cases. Low concentrations of ammonia were measured in the aerobic water, but not in the anaerobic. Turbidity varied with time, indicating dynamic processes in both stagnant seawaters. The microbial population of the bulk water varied with exposure condition (Table 4). Under anaerobic conditions the numbers of culturable anaerobic bacteria increased as indicated by the most probable numbers (MPN) of general anaerobic heterotrophs, APB and SRB. In the chamber maintained with exposure to air, all measured microbial populations decreased with time.

E_{corr} was monitored continuously for each of the 1020 carbon steel electrodes over the first 140 days in both the aerobic and anaerobic exposures. Figure 4 is representative behavior of four individual electrodes orientated vertically (side) and horizontally (bottom) in both exposure conditions. Data for four coupons are shown for clarity and due to the small differences in E_{corr} values for samples in the

same orientation and exposure type. E_{corr} values for all samples initiated at approximately -0.75 V (Ag/AgCl). Over the next 80 days, E_{corr} values for the aerobic condition in both orientations increased approximately 50 mV, while values in the anaerobic condition initially increased by 75 mV but then stabilized at approximately -0.75 V (Ag/AgCl). A notable difference between exposure conditions was the observation of small fluctuations of E_{corr} in the aerobic condition while the anaerobic condition remained smooth. At 80 days in the aerobic case, the fluctuations began to increase to almost 100 mV in amplitude. At 87 days, the datalogger malfunctioned and data were lost until 115 days at which time the fluctuations increased to almost 200 mV in amplitude. No appreciable difference in E_{corr} was observed between coupons in the vertical (side) and horizontal (bottom) orientations. In the case of the anaerobic exposure, between 60 and 110 days the horizontal (bottom) coupon E_{corr} began to increase to almost -0.7 V (Ag/AgCl) while the vertical (side) coupon E_{corr} remained at -0.75 V. Starting at 110 days, the E_{corr} values for both coupons in anaerobic seawater rose to -0.43 V (horizontal) and -0.48 V (vertical) in a 5 day span. Over the next 25 days, both samples E_{corr} values increased another 50 mV.

Linear polarization measurements were performed on individual electrodes in both exposure types over the 140-day exposure. The polarization resistance (R_p) was calculated for each sample and the R_p values were averaged into the four groups: aerobic side, aerobic bottom, anaerobic side, anaerobic bottom. The inverse was taken and plotted vs. exposure time (Figure 5) giving a value proportional to the instantaneous corrosion rate. After 23 days exposure, corrosion rates for all samples were relatively low with the lowest being the anaerobic case. However, after more than 100 days exposure, the $1/R_p$ measurements indicated that the highest instantaneous corrosion rate was measured in the horizontal (bottom) coupons exposed to anaerobic seawater. Weight loss data (Insert in Figure 5) demonstrate the same trends.

The appearance of the electrodes varied with exposure condition. Observations have been summarized in Table 5 and documented in Figures 6 and 7. The corrosion products that formed under aerobic and anaerobic seawater conditions were predictably different in appearance and composition.

Localized corrosion was more severe on the horizontally oriented sample than on the vertically oriented coupons in both exposure conditions. Bacteria were located within the corrosion products formed under aerobic and anaerobic conditions. The most conspicuous organisms in the corrosion products formed under aerobic conditions were filaments, often twisted and encrusted with iron oxides. The EDS spectra indicated iron oxides with traces of phosphorus and calcium and no sulfur could be detected in the corrosion products over the 6-month exposure, indicating the absence of a sulfide layer. After acid cleaning, an adherent layer of black iron oxide remained on the surface of the coupons exposed to aerobic seawater. Corrosion on the vertically oriented coupons was general in nature. Some pitting was observed on horizontally oriented coupons. Black corrosion products formed under anaerobic conditions were extremely uniform containing smaller microorganisms. In some cases the corrosion products contained 30% sulfur, in addition to phosphorus and iron. Corrosion on vertically oriented coupons was general in nature. Corrosion on the horizontally oriented samples produced a porous surface with some localized pitting.

DISCUSSION

Because anaerobic conditions and sulfides form within marine biofilms at biofilm/metal interfaces, independent of bulk oxygen concentrations, the impact of stagnant oxygenated and anaerobic seawater conditions on overall corrosion and corrosion rate are not so easily predicted. MIC of mild steel by SRB has been reviewed extensively.¹²⁻¹⁸ SRB within mixed species biofilms produce sulfide that reacts with iron to produce iron sulfides corrosion products that may be either protective or corrosive. When iron sulfides form a tightly adherent thin film, they are protective. However, iron sulfides are inherently unstable and their disruption can give rise to corrosion cells between the iron sulfide in direct electrical contact with the underlying steel (cathode) and the exposed-steel surface (anode). Several investigators have demonstrated maximum corrosion SRB corrosion in the presence of oxygen.^{8,9,15,17}

In his "unifying electron transfer hypothesis," Hamilton¹ reconciled apparently quite different microbiologically mediated corrosion processes. He concluded that the activities of microorganisms produced kinetically favored pathways of electron flow from the metal anode to the universal electron acceptor, oxygen. He observed that microbial ecosystems, including soils, sediments, water columns, and biofilms, are characterized by aerobic and anaerobic zones that operate as a continuum via redox couples within the ecosystem. Biofilms 75µm thick in aerobic media can produce anaerobic conditions at the biofilm/metal interface if the aerobic respiration rate is greater than the diffusion rate of oxygen into the biofilm.^{9,15} Hamilton and his co-workers^{12-14,18,20} were the first to demonstrate sulfide production by SRB within anaerobic niches of biofilms in oxygenated seawater. The interactions between oxygen and sulfate depend on redox cycling via intermediate electron carriers.

Hamilton¹ further stressed that biofilm growth is a dynamic process and the microorganisms within the biofilm are in a constant state of flux. Individual bacterial species and bacterial consortia are characterized by their primary energy source and electron donor and by the nature of the terminal electron acceptor. Oxygen is the terminal electron acceptor for aerobic species, but for anaerobic species there are alternate electron acceptors, e.g., nitrate, sulfate, ferric iron, CO₂. Carbon and energy flux in both individual cells and microbial ecosystem require electron transfer and metal ion oxidation/reduction.

Experiments reported in this paper demonstrate flux in the bulk water chemistry and bulk microbial populations and the complexity of corrosion reactions in the presence of a biofilm. The data further demonstrate that corrosion reactions from the same water source vary markedly with the exposure conditions.

CONCLUSIONS

In the experiments described in this paper, coupons exposed aerobically did not develop an anaerobic biofilm/metal interface as evidenced by the intact, tenacious iron oxide on the coupons. In

contrast, the coupons exposed anaerobically over the same period were covered with a sulfur-rich, non-tenacious layer of microorganisms in corrosion products. It is clear from the weight loss and R_p data that the anaerobic condition did not inhibit corrosion and that oxygen was not required for aggressive localized corrosion. It is also possible that the corrosion would have been even more aggressive in the presence of oxygen. The experiments will be continued for an additional six months.

ACKNOWLEDGEMENTS

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REFERENCES

1. W.A. Hamilton, *Biofouling* 19, 1, (2003): p 65.
2. P.F. Sanders, W.A. Hamilton, in *Biologically Induced Corrosion*, ed. S.C. Dexter, (Houston, TX, NACE, 1986), p. 47.
3. W.A. Hamilton, S. Maxwell, "Biological and Corrosion Activities of Sulphate-Reducing Bacteria within Natural Biofilms," *Biologically Induced Corrosion*, ed. S. C. Dexter, (Houston, TX, NACE, 1986), p. 131.
4. B.L. Little, F. Mansfeld, *Electrochim. Acta* 37, 12, (1992): p. 2291.
5. J.D.A. Miller, A.K. Tiller, *Microbial Aspects of Metallurgy*, (New York, Elsevier, 1970).
6. W.C. Lee, Z. Lewandowski, M. Morrison, W.G. Characklis, R. Avci, P.H. Nielsen, *Biofouling* 7, (1993): p. 217.
7. M. Eashwar, G. Subramanian, P. Chandrasekaran, K. Balakrishnan, in *Proc. Corrosion '90*, No. 120, (Las Vegas, NACE, 1990).
8. J.A. Hardy, J.L. Bown, *Corrosion* 40, (1984): p. 650.
9. W.C. Lee, Z. Lewandowski, S. Okabe, W.G. Characklis, R. Avci, *Biofouling* 7, (1993): p. 197.
10. B.J. Little, R.K. Pope, R. Ray, *Biofouling* 16, 2-4, (2000): p. 83.

11. ASTM G1 Designation C. 3.5, Annual Book of ASTM Standards, Volume 3.02, Wear and Erosion; Metal Corrosion, (West Conshohocken, PA., ASTM, 1994).
12. W.A. Hamilton, Microbially Influenced Corrosion in the Context of Metal Microbe Interactions, in Biofilms: Recent Advances in their Study and Control, ed. L.V. Evans, (Amsterdam, Harwood Academic Publishers, 2000) p. 419.
13. W.A. Hamilton, Microbially Influenced Corrosion in the Context of Metal Microbe Interactions, in Microbial Corrosion, ed. C. A. C. Sequeira, (London, European Federation of Corrosion, IOM Communications, 2000) p. 3.
14. W.A. Hamilton, W. Lee, Biocorrosion, in Sulfate Reducing Bacteria, ed. L.L. Barton, (New York, Plenum Press, 1995), p. 243.
15. W. Lee, Z. Lewandowski, P.H. Nielsen, W.A. Hamilton, Biofouling 8, (1995): p.165.
16. Z. Lewandowski, W. Dickinson, W. Lee, Water Sci. Technol., 36, (1997): p. 295.
17. P.H. Nielsen, W. Lee, Z. Lewandowski, M. Morrison, W.G. Characklis, Biofouling 7, (1993): p. 267.
18. P.F. Sanders, W.A. Hamilton, Sulphate-Reducing Bacteria and Anaerobic Corrosion, in: Corrosion and Marine Growth on Offshore Structures, eds. J.R. Lewis, A.D. Mercer, (Amsterdam, Harwood Academic Publishers), p. 23.

Table 1. Chemical composition of carbon steel 1020.

AISI-SAE designation	C	Mn	P max	S max	Fe
M1020	0.17-0.24	0.25-0.60	0.04	0.05	remainder

Table 2. Water chemistry in stagnant aerobic seawater.

Days Exposure	pH	Sulfide (ppm)	Sulfate (ppm)	Ammonia (ppm)	Nitrate/Nitrite (ppm)	Turbidity (NTU)*
0	8.02	<0.01	-	-	-	-
60	7.33	<0.01	3812	0.88	<0.6	5.38
95	7.37	0.06	3856	0.56	<0.6	4.89
125	7.22	0.39	3360	0.79	1.0	3.8
152	7.25	-	-	-	-	-

* NTU - Nephelometric Turbidity Units

Table 3. Water chemistry in stagnant anaerobic seawater.

Days Exposure	pH	Sulfide (ppm)	Sulfate (ppm)	Ammonia (ppm)	Nitrate/Nitrite (ppm)	Turbidity (NTU)
0	6.23	<0.01	-	-	-	-
48	6.79	0.52	3692	<0.2	3.1	6.39
83	6.72	0.74	3784	<0.2	0.8	27.4
113	6.91	0.49	3608	<0.2	<0.6	5.56
140	7.01	-	-	-	-	-

Table 4. Most probable numbers of bacteria.

	Aerobes (10) ^x	Anaerobes (10) ^x	APB (10) ^x	SRB (10) ^x
Raw Seawater (0 days)	4	3	4	0
Aerobic (60 days)	1	1	1	1
Anaerobic (48 days)	3	5	5	3

Table 5. Observations After Six Months

Operating Condition	Corrosion Products	ESEM/EDS	Description of Corrosion
Stagnant natural seawater, maintained in a covered container open to air	Reddish brown granular corrosion products on sides and bottom.	Corrosion products on sides and bottom contained filamentous cells with iron oxides. Sides and bottom had different appearance. Bottom granules finer and more uniform. Spalling on sides, but not on bottom	General corrosion on sides and bottom.
Stagnant anaerobic natural seawater, maintained in an anaerobic hood.	Black corrosion products with white crystals on sides and bottom.	Bacteria in corrosion products on both sides and bottom	General corrosion on sides and bottom. Isolated pitting on bottom.

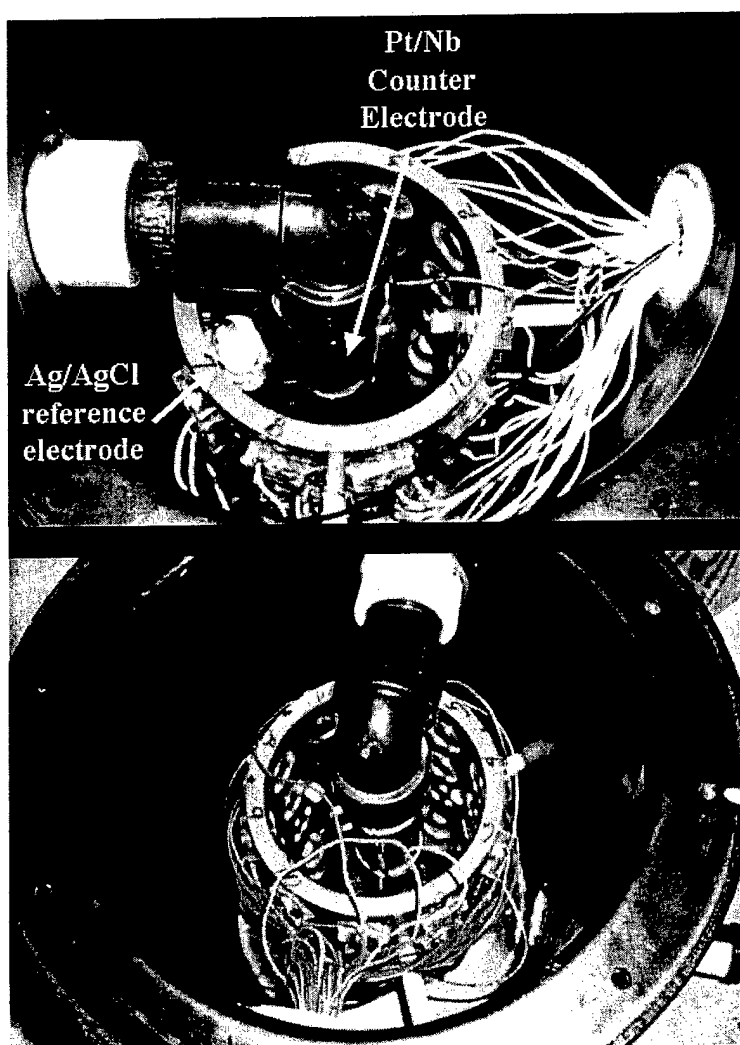


Figure 1. Experimental chamber.

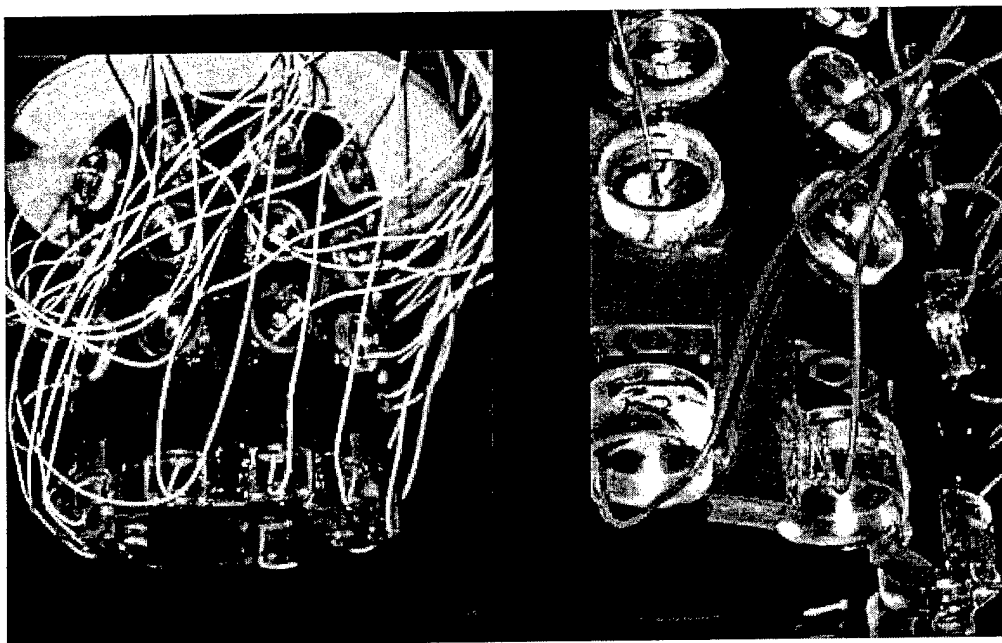


Figure 2. Electrode holder and individual electrodes orientated both horizontally (bottom) and vertically (sides).

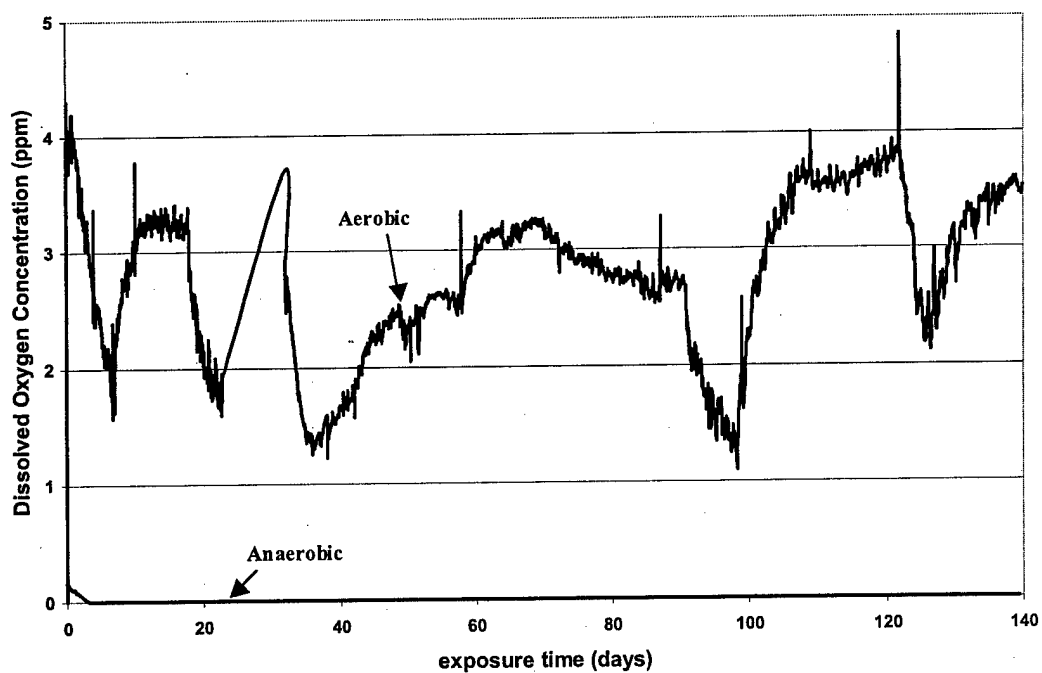


Figure 3. Dissolved oxygen concentration (parts per million, ppm) over time for both aerobic and anaerobic stagnant conditions.

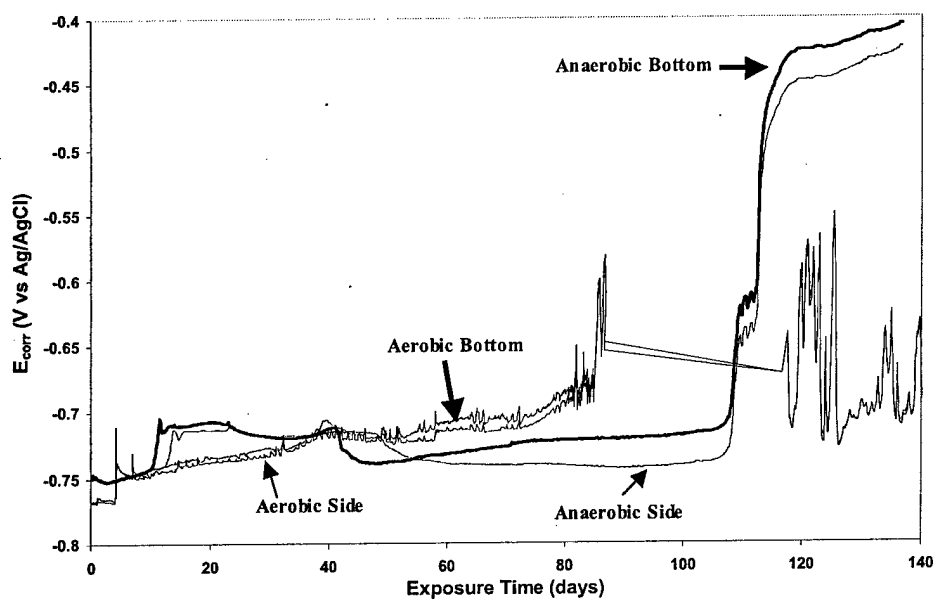


Figure 4. Representative E_{corr} (vs. Ag/AgCl) over time values for horizontally (bottom) and vertically (side) orientated C1020 samples in stagnant aerobic and anaerobic conditions.

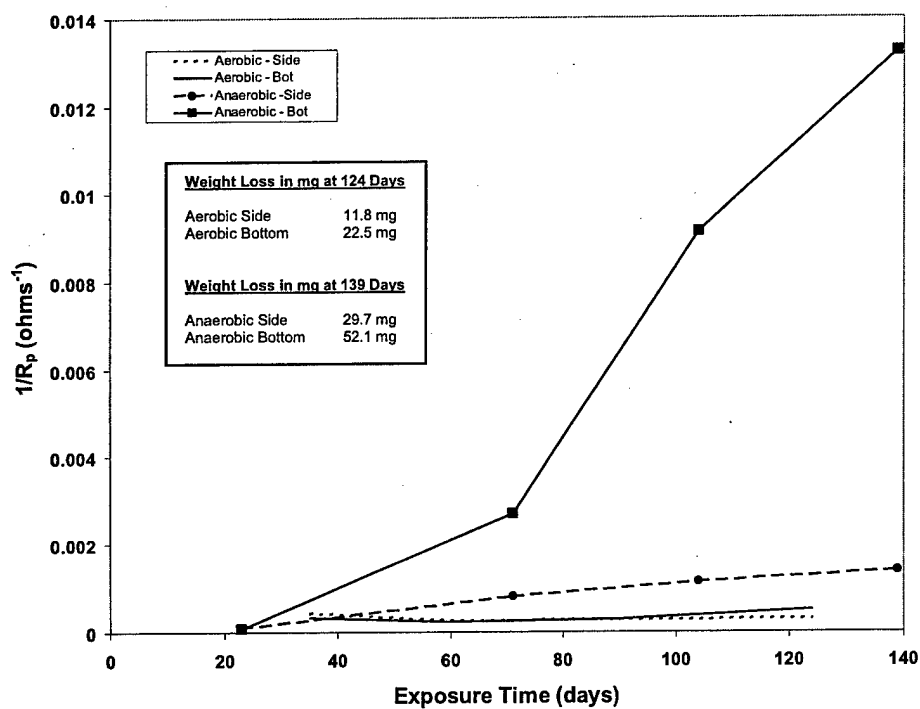


Figure 5. Average R_p over time for horizontally (bottom) and vertically (side) orientated C1020 samples in stagnant aerobic and anaerobic conditions. Insert includes weight loss data of samples from the aerobic condition (124 days exposure) and the anaerobic condition (139 days exposure) for both orientations.

Vertical Orientation

Horizontal Orientation

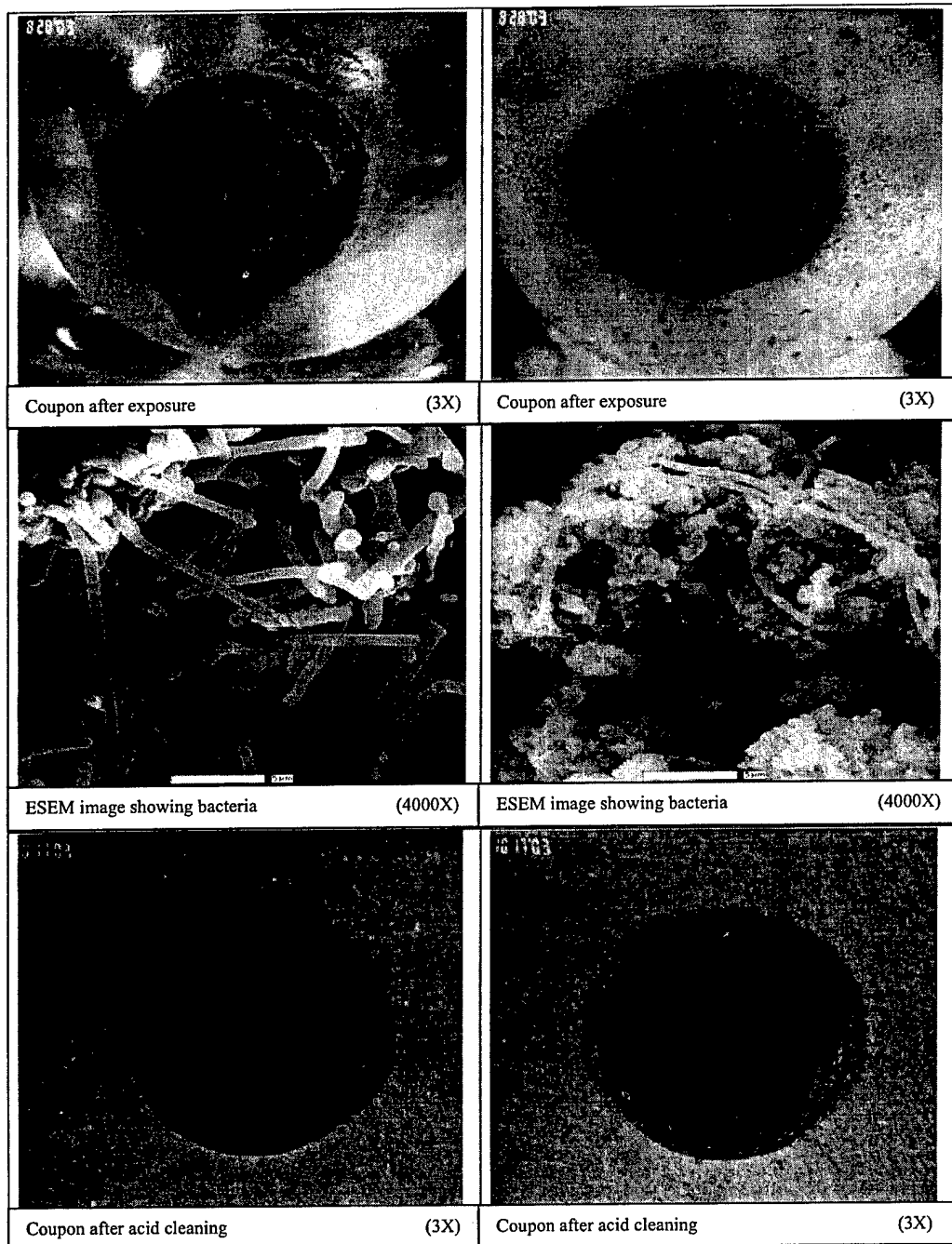


Figure 6. Photos and micrographs of C1020 samples exposed to stagnant aerobic natural seawater for 124 days.

Vertical Orientation

Horizontal Orientation

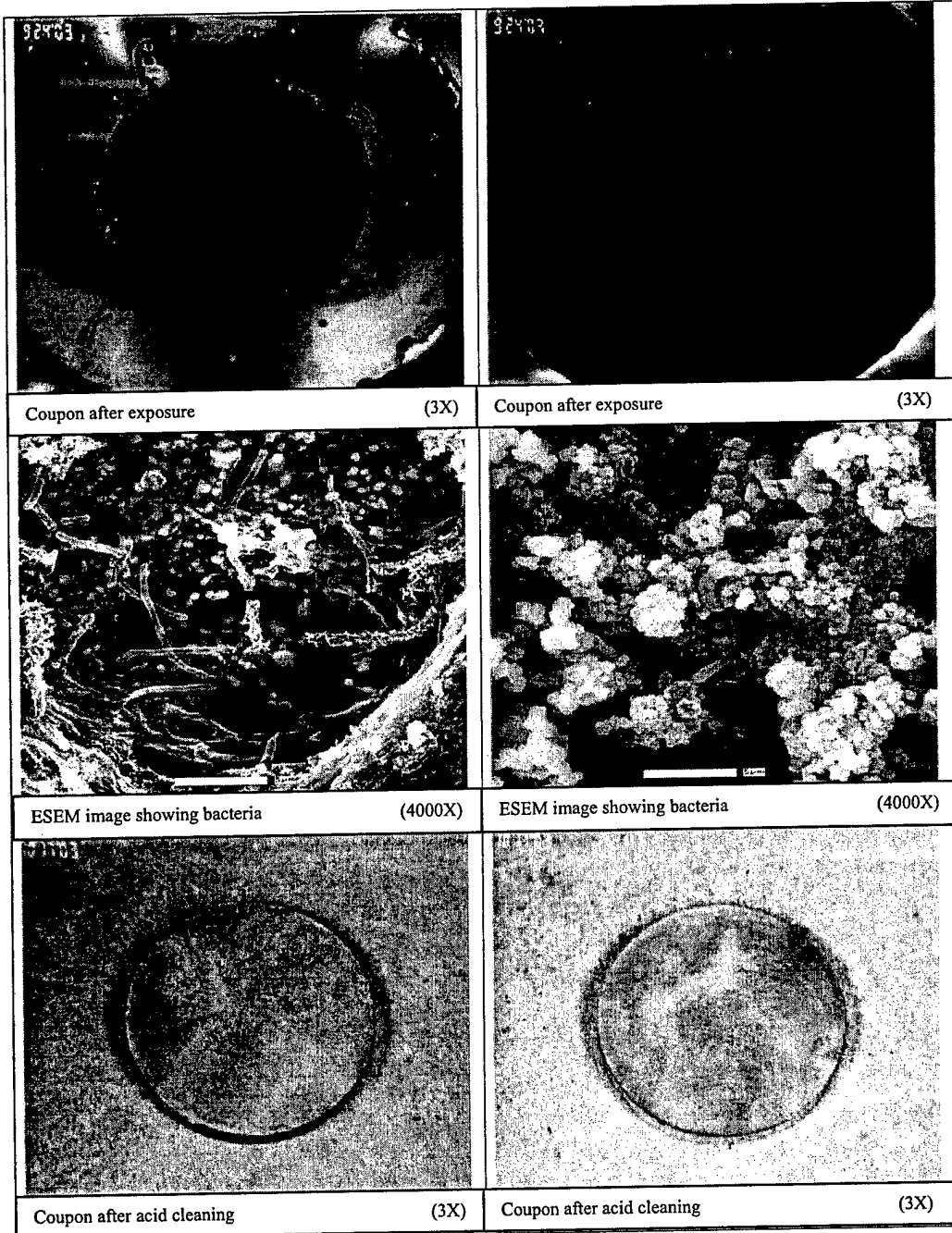


Figure 7. Photos and micrographs of C1020 samples exposed to stagnant anaerobic natural seawater for 139 days.